Electrochemistry at the tracer scale - an approach to aqueous superheavy element chemistry

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Due to the recent successful gas-phase experiments with hassium [1, 2] and element 112 [3] the focus of aqueous heavy element chemistry shifted also in that region of the periodic table. Theoretical predictions by Fricke et al. [4] suggest, that the superheavy elements 112-118 have a noble metal character. These predicted properties led to an electrochemical approach for first aqueous studies of the superheavy elements. The electrochemical deposition of tracer amounts on a metal surface usually does not lead to a complete coverage of the electrode. Such sub-monolayer electrodepositions cannot be described by the Nernst equation and may take place at more negative (overpotential deposition, opd) or at more positive potentials (underpotential deposition, upd), depending on the properties of tracer and electrode material. Using macroscopic thermodynamic models, Eichler et al. proposed a modified Nernst equation to describe the electrodeposition of tracer amounts on a given electrode material [5]. They calculated potentials for the deposition of 50% of the tracer ion on a foreign electrode material. In an earlier work, $E_{50\%}$-values of the elements 112-116 were predicted on the basis of relativistic Dirac-Slater calculations [6]. Pd- and Pt-systems have the highest $E_{50\%}$-values and should be preferable electrode materials for electrodeposition experiments. To design an electrochemical deposition experiment for super-heavy elements, we have to investigate how the predicted $E_{50\%}$-values correspond to experimental upd-potentials for the homologs of the elements 112-116 and if a spontaneous deposition of the tracer is possible. Furthermore, we have to figure out what kind of electrode pretreatment is necessary to achieve a clean surface and - due to the very short half-lives of the superheavy isotopes - how a quantitative electrochemical deposition can be performed in a very short period of time. In the first batch experiments with the lighter homologs of the superheavies, we kept our focus on lead (homolog of 114) and polonium (homolog of 116) because carrier free trace amounts of those elements were easy to obtain. ^{212}Pb was obtained via electrostatic gas phase collection of the decay products from a ^{220}Rn emanating source (^{228}Th co-precipitated with Zr-Stearate), whereas ^{210}Po was extracted from irradiated bismuth by ion-exchange chromatography. Already the first experiments, especially with lead, showed, that the spontanous electrodeposition is a relatively slow, diffusion controlled process. Therefore, we continued the work on two different paths. The lead experiments were now performed under a controlled potential using standard electrochemistry equipment. The polonium studies, on the other hand, continued to look into the involved parameters for the spontanous deposition. Reproducible results in electrochemical experiments can only be achieved by using electrodes with very clean surfaces. To get such electrodes, a first procedure was established, where the electrodes (metal foils) are cleaned by heating under an argon/hydrogen (95:5) atmosphere at about 700K to remove oxides from the surface. Using a 0.1M HCl solution of ^{210}Po, a series of experiments on the spontanous electrodeposition of Po has been performed. During these studies a range of parameters was varied. The experiments used Cu, Ag and Ni in form of 6x6mm foils as electrode materials. These foils were introduced into a small electrochemical cell with a volume of only 200µl [7].To get information about the influence of the solvent and its dielectric properties on the deposition process, mixtures of ^{210}Po in 0.1M HCl with organic solvents (acetone, dioxane) were used. To assure a maximum ion motion towards the electrode, the cell was heated to 340K and treated with ultrasound. In these experiments, relatively long reaction times of 5min and 1min were chosen. The determination of the amount of deposited Po was performed by α-spectroscopy.
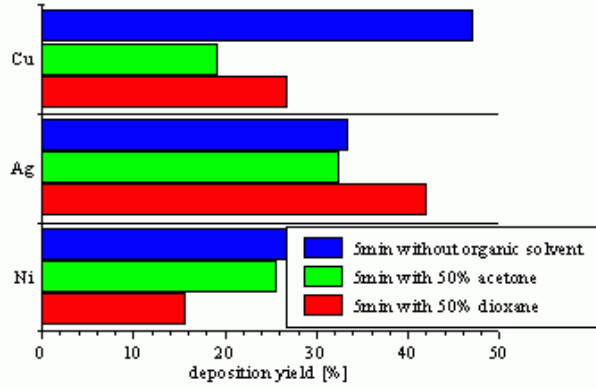
Fig.1: Deposition yields of Po-210 from 0.1M HCl on Cu, Ag and Ni
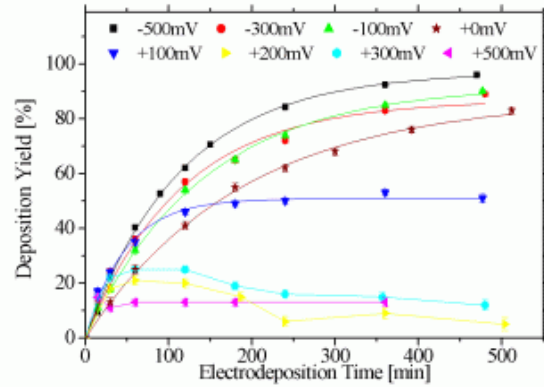

Fig.2: Electrodeposition of Pb on a Pt-electrode in 0.1M HCl vs. time at different potentials

The measured deposition yields (figure) did not show any clear trend with respect to the variation of the reaction time and the change in solvent characteristics. This result can only be attributed to variations in the properties of the electrode surface. Thus, the used cleaning process might still be not sufficient to get reproducible results. As an alternative cleaning process, an electrochemical treatment will be used, where the electrode is cleaned by a quick electrolysis process. After that, it will be stored in a solution of the electrolyte used in the later experiments. This process should prevent the surface from being exposed to air and therefore from being contaminated with oxygen and aerosol particles. Hevesy and Paneth defined the "critical potential" E_{crit} as the potential, at which electrodeposition of a radiotracer on a metal electrode first occurs [8]. Obviously, measured E_{crit}-values should be similar to the predicted $E_{50\%}$-values. To determine the critical potential of the Pb-upd on Pt electrodes, we used a potentiostatic three-electrode-system with a Ag/AgCl (3M KCl) reference electrode, a Pt working electrode, and a Pt counter electrode. The area of the working electrode was 2cm², the total volume of the 0,1M HCl electrolyte solution was 20ml. For agitation, we applied a constant nitrogen flow. Prior to the experiment, the working electrode was electrochemically cleaned. To determine the deposition yield of ^{212}Pb vs. the electrodeposition time without disturbing the system, we measured the decrease of the activity in the solution by γ-spectrometry. The experiment was repeated at different electrode potentials. According to Joliot [9], the electrodeposition rate of a radiotracer is described by

$$dN_{dep}/dt = DF_E/\delta V * (kN_{tot} - N_{dep}). \quad (1)$$

After integration, a relation between the deposition yield N_{dep}/N_{tot} and the reaction time is obtained

$$N_{dep}/N_{tot} = k - k * \exp(-DF_E/\delta V). \quad (2)$$

Here, N_{dep} is the amount of atoms deposited, N_{tot} is the total amount, D is the diffusion coefficient, F_E is the electrode surface, δ is the Nernst diffusion layer and V the volume of the solution. The term k represents the maximum deposition yield that can be reached for the given potential E. In the experiment, we obtain a relation between the deposition yield and the electrodeposition time (Fig.2). After fitting with equation 2, we get the maximum deposition yield k for each potential E (Fig.3). The critical potential E_{crit} for the deposition of Pb on Pt from 0.1M HCl is about +190mV. This value corresponds roughly to the critical potential of +255mV for the deposition of Pb on Pt in 1N HNO_3 measured by Ziv et al. [10]. The predicted $E_{50\%}$-value of +10mV [5] is somewhat lower than the measured E_{crit}-value, but the difference gets smaller if compared with the potential at which the maximum deposition yield is 50% (approx. +100mV).
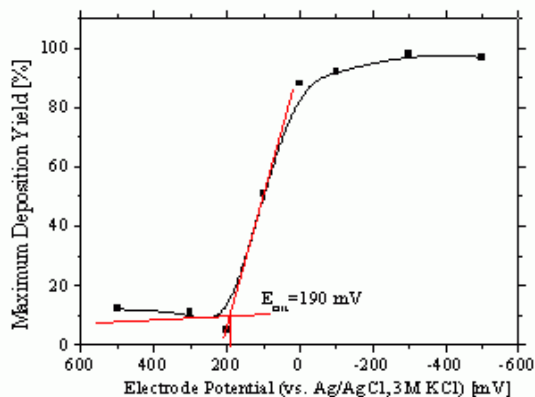
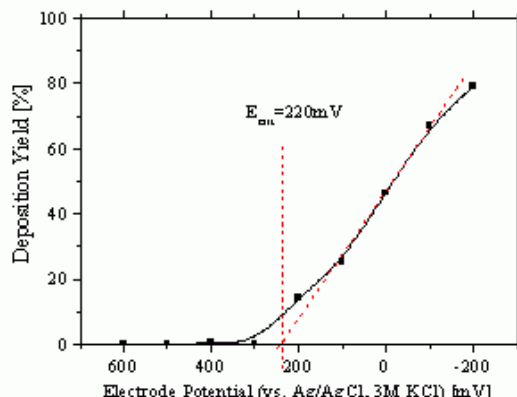Fig.3: E_{crit} for the Pb-upd on Pt-electrodes in 0.1M HCl

Fig.4: E_{crit} for the Pb-upd on Pd-electrodes in 0.1M HClO$_4$

According to equation (1), the electrodeposition rate dN_{dep}/dt increases with F_E/V. As a consequence, we reduced the dimensions of the electrolytic cell to a total volume of 150µl and an electrode surface of 0.36cm². The deposition rate also depends on the thickness of the Nernst diffusion layer. To keep it low, we agitated the solution with a magnetic stirrer. As reference electrode, we used a micro-Ag/AgCl-electrode. In this experiment, we used Pd as electrode material, and the electrolyte was 0.1M HClO$_4$. Compared to the "macro-expriment" described above, the electrodeposition rate increased - as calculated - by a factor of 24. After 10 minutes, the deposition yield is near to its maximum possible value. After the deposition, the electrode was removed while under current, washed with water and measured on a γ-detector. No activity was lost during the washing process. Fig.4 shows, that no activity is deposited until the critical potential of about +220 mV is reached. From this point on the deposition yield increases with the applied potential. The critical potential we determined in the Pb/Pd-system is similar to that in the Pb/Pt - system. However, a remarkable difference between the two systems is, that the deposited activity can be easily removed from Pt-electrodes by mineral acids, but not from Pd-electrodes. In future experiments, we will further improve the electrolytic cell dimenstion to obtain reaction times in the range of seconds. For online experiments at the Mainz TRIGA reactor and at GSI, an automated apparatus using a tape technique to provide the electrode material is planned. This device will combine the electrode cleaning step, the electrochemistry step, and the detection system.

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